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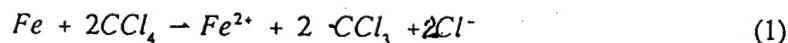
PROCESSES AFFECTING REDUCTIVE DECHLORINATION
OF CHLORINATED SOLVENTS BY ZERO-VALENT IRON

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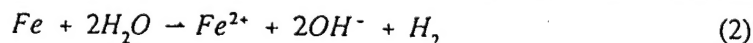
In a study of groundwater sampling, Reynolds *et al.* (1990) reported that several halogenated hydrocarbon solvents were unstable in the presence of metallic well casings. Further investigations, involving laboratory and field experiments, indicated that zero-valent (metallic) iron rapidly dehalogenated a variety of halogenated solvents. (O'Hannesin and Gillham, 1992). Since iron is relatively inexpensive and non-toxic, it was proposed that this process could be useful for the *in situ* remediation of contaminated groundwaters. An in-ground permeable barrier based on this idea is currently being tested in the field and seems to be showing considerable promise. However, further improvement of this technology is hindered by the lack of information on 1) the mechanism and kinetics of dechlorination by iron and 2) the microbial and geochemical processes that may influence the performance of this technique in the field. The goal of our research is to provide a comprehensive survey of the mechanisms that affect the performance of this reactive barrier technology.

Zero-valent iron may participate in the reductive dechlorination process by three different mechanisms: direct, electrolytic reduction; reduction by hydrogen produced during the corrosion process; and reduction by dissolved (ferrous) iron that is also produced by corroding iron. The first step of electrolytic reduction is, presumably, the transfer of one electron from the metal surface to the organic molecule. This results in an organic anion radical that may then lose a halide anion to give a carbon-centered radical, and oxidized iron, which is eventually released to the solution as Fe^{2+} .



The carbon-centered radical may go on to react in a variety of ways, including sequential dehalogenation, coupling, and hydrolysis (Criddle and McCarty, 1991). In an effort to study this process we have set up laboratory model systems containing granular iron that were prepared anaerobically in serum bottles, with no headspace, and sealed with septa inert to chlorinated solvents. Decrease of substrate concentration and appearance of dechlorination products were monitored by GC/FID with whole column cryotrapping. Representative results from these experiments are shown in figure 1.

Dechlorination can also occur by reduction with the hydrogen that is formed during the corrosion process.



Hydrogen alone is not a facile reductant of chlorinated hydrocarbons, but in the presence of a catalyst it could cause rapid dehalogenation. Iron, or other surfaces, could provide the catalyst, and so this process has not been ruled out as a possible contributor to the dechlorination reaction. Experiments designated to test the role of H_2 in this process are currently in progress.

Ferrous iron may also contribute to dechlorination of the carbon tetrachloride. As shown in reaction 2, ferrous iron is released during the corrosion of metallic iron. Laboratory and field experiments show that large amounts of ferrous iron are released (5 - 10 mg/L). Under these conditions abiotic dechlorination by dissolved iron is also possible. The importance of this process will be dictated by the presence and type of ligands in the system since the speciation of the ferrous iron dramatically affects its strength as a reductant. Our laboratory experiments to date indicate no significant dechlorination by ferrous iron alone and experiments with complexed iron are in progress.